Lewis acid catalysis of a Diels-Alder reaction in water

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Lewis-Acid Catalysis of a Diels-Alder reaction in water.

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Second-order rate constants ($M^{-1}s^{-1}$) of the Cu^{2+}-catalyzed DA reaction of **1a**, **1b**, **1d** and **1e** with **2** in different solvents at 25°C.

Solvent	**1a**	**1b**	**1d**	**1e**
acetonitrile	2.21	0.594	0.240	0.0689
ethanol	0.769[a]	0.382	0.162	0.0510
water	3.25	1.23	0.654	0.262
2,2,2-trifluoroethanol	15.6	3.31	1.52	0.549

(a) This value deviates from the otherwise linear Hammett-plot. In the Hammett correlation the rate constant for **1** with X=CO_2CH_3 (k_2=0.655 $M^{-1}s^{-1}$) was used instead.

Equilibrium constants from complexation of **1a**, **1b**, **1d** and **1e** with different metal ions (K_a) and second-order rate constants for the DA reaction of these complexes with **2** (k_2) in water at 2.00 M ionic strength and 25°C.

	Co^{2+}		Ni^{2+}		Cu^{2+}		Zn^{2+}	
	K_a	k_2	K_a	k_2	K_a	k_2	K_a	k_2
1a	86.9	$2.84\cdot10^{-1}$	318	$5.69\cdot10^{-1}$	425	11.1	34.5	$5.03\cdot10^{-1}$
1b	112	$1.02\cdot10^{-1}$	579	$1.18\cdot10^{-1}$	1059	2.82	57.3	$1.22\cdot10^{-1}$
1d	127	$4.67\cdot10^{-2}$	947	$4.61\cdot10^{-2}$	1553	1.36	88.1	$5.81\cdot10^{-2}$
1e	178	$2.11\cdot10^{-2}$	1496	$1.91\cdot10^{-2}$	2759	0.518	161	$2.48\cdot10^{-2}$